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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the Production of Valuable Oxidation Products from Aliphatic Hydrocarbons

We, HENKEL & CIE., G.M.B.H., a German Company, of 67, Heyestrasse, Düsseldorf-Holthausen, Germany, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

In the oxidation of high-molecular aliphatic hydrocarbons, it is known that a mixture of fatty acids, alcohols, esters, lactones and unoxidised hydrocarbons is obtained. Considerable difficulties are encountered in the treatment of this mixture.

It has now been found that particularly valuable oxidation products, such as high-molecular carboxylic acids may be obtained in a good yield by the following combination of treatment steps: treating the hydrocarbons with oxidising agents, fresh material being continuously supplied, continuously saponifying a portion of the oxidised material with alkaline agents, continuously separating the unsaponifiable matter from the saponified matter by centrifuging, and submitting it to an oxidation again. In this way, it is possible to adhere to a definite (even mild) oxidation stage in the reaction chamber.

The new process may be employed for the oxidation of many kinds of higher aliphatic hydrocarbons and their natural or artificial mixtures. Natural or artificial solid and liquid paraffins such as soft paraffins, hard paraffins, furthermore hydrocarbon mixtures of the various benzine syntheses come into consideration as starting materials. For example, the liquid-solid mixture of higher aliphatic hydrocarbons, such as is obtained in the treatment of synthetic benzine according to Franz Fischer (see "Brennstoff-chemie", 1928, page 21 and 1932 pages 461 *et seq.*) is suitable.

The oxidation of the higher aliphatic hydrocarbons may be effected by processes known *per se*. The oxidation may be carried out for example with oxygen, gases which contain oxygen or compounds which give up oxygen, such as ozone, oxides of nitrogen or the like, in the presence or absence of catalysts such as heavy metals or their salts, for example manganese, cobalt, copper, iron, chromium, lead or vanadium or even aluminium salts, and also in the presence or absence of alkalis, alkaline earths or their salts. The said metals may also be present in the form of soaps of the saturated or unsaturated fatty acids, naphthenic acids or resinic acids which dissolve colloidally in the hydrocarbon mixture.

The oxidation is carried out for example in a cylindrical vessel. The agitation of the reation material in some cases is effected sufficiently even by the gas which is being passed therethrough. It is however possible to employ also an additional stirring device, such as a vane rotor.

The choice of the temperature depends upon the starting material and the oxidising agent, and generally lies between 90° and 200° C. The reaction proceeds exothermally and therefore, if necessary, it must be continued with the application of cooling, for example by a cooling coil. A heating device, for instance a steam coil or an electric heating device, is provided for initiating the reaction. An automatic temperature regulating device may be provided in order to facilitate continuous operation.

An intensive mixing of the liquid reaction material with the oxidising gases takes place within the reaction vessel. The gases enter the reaction chamber, for example from tubes having a large number of fine holes or from porous plates. Alternatively, however, it is also possible to spray the reaction material in the gas chamber. If desired, the gas may be introduced under pressure and the reaction vessel may be constructed after the manner of an autoclave.

The catalysts are added separately or together with the fresh, if desired preheated, unoxidised hydrocarbons. Since, if a certain proportion of oxidised material is already present, the oxidation proceeds at a sufficient rate without the addition of catalysts, it is possible in the present continuous process to dispense with the subsequent addition of catalysts. The use of

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catalysts may be obviated entirely if, at the commencement of the process, partly oxidised material is introduced into the oxidation chamber or if the reaction is first carried out during a sufficient length of time to produce such material.

By varying the rate at which the material enters and leaves the reaction vessel and the size of the latter, and by varying the temperature and the nature of the movement, the desired oxidation stage may be adjusted. This is checked, for example, by determining the saponification number of test samples.

Oxidised material from the oxidation chamber is supplied continuously to a saponifying plant. Caustic soda or caustic potash or soda lye or potash lye or if desired alkali carbonates or lime are employed for saponification. In order to carry out the saponification rapidly, it is preferable to employ an elevated temperature and, if desired, pressure. The oxidation products may be passed through a plurality of saponification plants in succession or they are distributed beforehand among a plurality of saponification plants. The volatile components escaping during saponification are condensed or absorbed and if desired they are returned to the oxidising chamber.

The saponified reaction mass is fed to a centrifugal machine, possibly after previous dilution with water and if desired after filtration or other preliminary treatment. Centrifugal machines of every possible type, in particular powerfully acting high-speed centrifugal machines may be employed. The oxidation products are advantageously fed to the centrifugal machines while in the still hot condition. The centrifugal machines effect a separation of the liquid layers or the deposition of the solid substances. If necessary, the reaction material is passed through a plurality of centrifugal machines in order to make the separation still more complete. The separated unsaponifiable matter is returned continuously to the oxidation chamber.

The separated soap, which contains small proportions of unsaponifiable matter, may be treated in various ways. The unsaponifiable material may be extracted, for instance, by treatment with solvents in a manner known *per se.* Furthermore, the soap may be concentrated by evaporation and dried and then freed from the unsaponifiable matter by means of solvents such as acetone or ethyl acetate. Another method is to separate the unsaponifiable matter from the dried soap by vacuum distillation with or without steam. All these processes may likewise be continuous. The unsaponifiable portions separated from the saponified material are likewise returned to the oxidation chamber.

Apart from the fact that in itself it is very valuable to carry out the oxidation of paraffins and the treatment of the oxidation products continuously, it is possible by means of the process employed according to the invention to adjust a definite oxidation stage and to effect a controlled oxidation. A good yield of valuable substances is obtained.

The arrangement of a plant in which the new process can be carried out will be gathered from the accompanying diagrammatic drawing. The hydrocarbons are introduced into a supply container A and are heated to above their melting point by means of the steam coil B. Through the steam-heated pipe C, in which they are heated to reaction temperature, the hydrocarbons pass to the oxidation chamber D, where air in a fine state of division is injected through the pipe E. The vane rotor F located in a cylinder G effects a circulation in the manner indicated. The vessel may be heated by the steam coil H and may be cooled by a water-cooling device. The escaping volatile constituents are separated in the condenser K. From the vessel D the reaction material passes successively through the three saponifying vessels L_1, L_2 and L_3, which are provided with stirring devices and are steam-heated (M_1, M_2, M_3). From the supply vessel N soda lye flows continuously to the reaction material in the vessel L_1. The product passes from the saponification vessel L_3 to the centrifugal machine O. The unsaponified material is pumped back into the oxidation vessel D through the pipe-line P. The saponified material passes to the thin layer evaporator Q and thence to the extraction plant R, where the dry soap is obtained continuously. The extracted unsaponifiable matter on the other hand after separation of the solvent is returned to the oxidation chamber D through the pipe-line S.

Example:

In an oxidation vessel of the kind described, 3600 parts by weight of a synthetic paraffin mixture which at the ordinary temperature is a partly liquid, partly solid mass, having a boiling point 270° to 360° C. is heated to a temperature of 105° to 115° C. with the addition 0.1% of manganese palmitate. Air is passed through the reaction liquid at the rate of 0.07 cubic metre per hour for each kilogram of paraffin mixture. When after a considerable time, the mixture has the saponification number 60, the continuous process is commenced. Then 100 parts by weight of the oxidised material is drawn off per hour. Unoxidised hydrocarbons flow continuously from a supply container heated to 40° C., and in the supply pipe they are pre-heated to the reaction temperature of ca. 110° C. The supply is regulated by an automatic device so that the level in the oxidation vessel always remains the same. The oxidised material drawn off flows to a vessel provided with powerful stirring devices and heated to 110° C. Soda lye continuously enters the vessel at such a rate that 13.2 parts by weight of soda lye (38° Bé) enter per 100 parts by weight of oxidised material. To complete the saponification, the mixture flows through two further heated vessels provided with stirring devices. The saponified material is then passed through a high-speed centrifugal machine while still hot, 75 parts by weight of unsaponifiable matter being recovered from 100 parts by weight of the oxidised material and returned to the oxidation chamber. In addition, a soap solution is obtained which contains about 15 parts by weight of saponifiable matter and 8 parts by weight of unsaponifiable matter per 100 parts by weight of the material leaving the oxidation chamber. This product is passed through a thin layer evaporator and after drying is continuously extracted with acetone. Thus, on the one hand, a soap is produced which may be used for many technical purposes and, on the other, the rest of the unsaponifiable matter, which after separation of the acetone is continuously pumped back to the oxidation vessel.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of valuable oxidation products from higher aliphatic hydrocarbons, characterised in that the hydrocarbons are treated with oxidising agents while fresh material is continuously supplied, a portion of the oxidised material is continuously saponified with alkaline agents, the unsaponifiable matter is continuously separated from the saponified matter by centrifuging and is again subjected to oxidation.

2. A process as claimed in claim 1, characterised in that the unsaponifiable constituents still contained in the saponified portion after centrifuging, if desired after previous evaporation of the soap solution, are separated from the saponified constituents by extraction with solvents or by distillation and are returned continuously to the oxidation chamber.

3. Apparatus for carrying out the process as claimed in claims 1 or 2, comprising an oxidation vessel, a saponification plant connected therewith and followed by a centrifugal machine unit which, for returning the unsaponifiable matter, is in communication with the oxidation chamber, the centrifugal machine unit being followed if desired, for the purpose of separating the rest of the unsaponifiable matter from the soap, by an extraction or distillation plant which is likewise in communication with the oxidation chamber.

4. The process and apparatus for the production of oxidation products from higher aliphatic hydrocarbons substantially as described with reference to the foregoing example.

Dated this 26th day of January, 1937.

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Reference has been directed, in pursuance of Section 7, sub-section (4), of the Patents and Designs Acts, 1907 to 1932, to Specifications numbered 434,311, 324,189, and 303,560, and in pursuance of subsection (5) to U.S.A. Specification No. 1,987,208.

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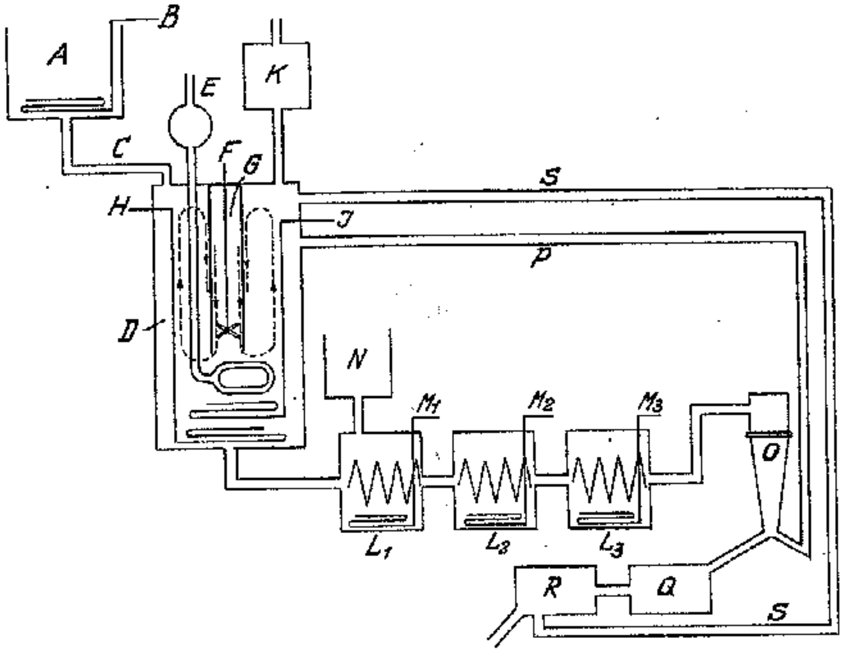
[This Drawing is a reproduction of the Original on a reduced scale.]



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